



Mechanism study on catalytic oxidation of chlorobenzene over $Mn_xCe_{1-x}O_2/H$ -ZSM5 catalysts under dry and humid conditions

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ABSTRACT

Developments on advanced catalysts for catalytic oxidation of chlorinated hydrocarbons still encounter bottlenecks in Cl^\bullet deactivation, low HCl and CO_2 selectivity, toxic by-products generation, etc. In this paper, a well-reported $Mn_xCe_{1-x}O_2$ catalyst was selected as active phase to access the role of H-ZSM5 in catalytic oxidation of chlorobenzene (CB) under both dry and humid conditions. The HCl and CO_2 production, by-products generation and CB oxidation routes variation were evaluated by using a range of analytical techniques including XRD, BET, GC/MS, in situ DRIFT, Ion Chromatography, etc. It was noted that the presence of H-ZSM5 could induce ca. 90% CB conversion at ca. 230 °C. However, only 20% CB was converted into CO_2 . There were nearly 25 by-products being detected in the off-gas. In situ DRIFT analyses revealed that under dry condition, the H-ZSM5 could promote Cl^\bullet dissociation from the aromatic ring of CB, which transferred the CB into cyclohexanone or benzoquinone species, hence facilitating CB ring-opening process. Under humid condition, the presence of H_2O could not only protect the active sites of $Mn_{0.8}Ce_{0.2}O_2$ from accumulated chlorine poisoning but also act as H^\bullet and OH^\bullet radical source to deeply oxidize CB, promoting the HCl and CO_2 production over the $Mn_xCe_{1-x}O_2/H$ -ZSM5 catalyst.

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1. Introduction

Chlorinated hydrocarbon is a kind of volatile organic compounds (VOCs) generated from a wide range of industrial processes and the incineration of domestic garbage and medical wastes [1–3]. It can cause serious health and environmental issue due to the persisted high toxicity and difficulty in natural degradation, which hence requires effective control on emission [4–8]. Catalytic oxidation has been considered as a promising technique for complete conversion of chlorinated hydrocarbons into relatively harmless CO_2 , H_2O and HCl. However, this technique has encountered challenges in developments of high-performance and reliable catalysts for practical application [1,9,10]. Although many of current works have shown their catalysts with high activities in chlorinated hydrocarbon oxi-

dation, the Cl^\bullet deactivation, low HCl and CO_2 selectivity and toxic by-products generation still remain a big issue for these catalysts.

Noble metal catalysts (e.g. Pt) have shown the ability in effective oxidation of chlorinated hydrocarbons but the trend to form volatile inorganic chlorides can cause quick deactivation for these catalysts [11–13]. Metal oxides (e.g. CeO_2) are reported able to achieve high performances in chlorinated hydrocarbons oxidation [14–16], ascribing to their significant abilities in breaking C–Cl bond. However, they also tend to be deactivated due to the coverage of dissociated Cl^\bullet on their active sites [17,18]. Recently, acid solids (e.g. H-Y, H-ZSM5, H-MOR and H-BETA) with abundant Brønsted and Lewis acid sites have been paid tremendous attentions due to their abilities in promoting oxidation activity and chlorine poisoning resistance for supported catalysts. Taralunga et al. found that a distinct promotion in oxidation activity could be achieved in the presence of HFAU for catalytic oxidation of chlorobenzene (CB) and 1,2-dichlorobenzene [6,19–22]. Scirè et al. reported that such promotion was strongly relied on the type of acid solids used where the H-ZSM5 as a carrier for Pt could show a much better performance than the H-BEAT and alumina in CB oxidation [23,24]. Furthermore, the H-ZSM5 is also able to promote the HCl selectivity through a dehydrochlorination of Cl^\bullet over the SiOHAi hydroxyl

Abbreviations: VOCs, volatile organic compounds; CB, chlorobenzene; H-ZSM5, zeolite socony mobile-five; DRIFT, diffuse reflectance infrared fourier transform; IC, ion chromatography; GHSV, gaseous hourly space velocity; BE, binding energy.

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[2,25]. Although current works in literature have demonstrated the promising roles of acid solids in catalytic oxidation of chlorinated hydrocarbons, the insights into by-products generation, HCl and CO₂ production and chlorinated hydrocarbons oxidation routes variation as resulted by the acid solids are still rare.

In this paper, a well-reported Mn_xCe_{1-x}O₂ catalyst [1,26,27] was selected as active phase to access the role of H-ZSM5 in catalytic oxidation of chlorobenzene (CB). The HCl and CO₂ production, by-products generation and oxidation routes variation were investigated by using a range of analytical techniques, including GC/MS, in situ DRIFT, ion chromatography, etc. The CB oxidation routes over Mn_xCe_{1-x}O₂ and Mn_xCe_{1-x}O₂/H-ZSM5 catalysts in the presence of H₂O or not were extensively evaluated.

2. Experimental

2.1. Syntheses

H-ZSM5 (with an appropriate Si/Al ratio at 30 [28,29]) was supplied from Zhiyuan Molecular Co., Ltd (Shanghai, China). The loading of Mn_xCe_{1-x}O₂ (at 20% in mass ratio) onto the H-ZSM5 were conducted via a wet impregnation route, whereas accurately measured Mn(NO₃)₂, Ce(NO₃)₃ and zeolite were mixed in an ethanol, followed by continuous stirring for 5 h. The mixture was then dried at 110 °C for 10 h and calcinated at 550 °C for 5 h in static air. The resulted products were denoted as Mn_xCe_{1-x}O₂/H-ZSM5, where x was 1, 0.8 and 0, respectively.

Mn_{0.8}Ce_{0.2}O₂ catalyst was synthesized via a hydrothermal route whereas an aqueous solution containing proper amounts of Mn(NO₃)₂, Ce(NO₃)₃ and citric acid (citric acid/(Mn + Ce) = 0.3 in molar ratio) was continuously stirred for 2 h at the temperature of 50 °C. Thereafter, the mixture was dried at 110 °C for 10 h and calcinated at 550 °C for 5 h in static air to yield final product.

The aforementioned metal salts (>99.9%) were all supplied from SCRC (Sinopharm Chemical Reagent Co., Ltd) and used as obtained.

2.2. Characterizations

Powder X-ray diffraction were recorded by using a Riga ku D/max-2500 powder diffractometer with Cu K α radiation at the voltage of 40 kV (XRD: D/max model RA, Riga ku Co., Japan; Cu K α radiation at 0.15418 nm). The data were collected at the scattering angles (θ) ranging from 10 to 80° with a step size of 4°.

BET surface area measurements were conducted by using a static volumetric adsorption analyzer JW-BK132F. Prior to measurement, all samples were degassed at 300 °C for 2 h in vacuum.

2.3. Activity measurements

Catalytic activities were measured in a fixed-bed reactor, in which 1000 mg of Mn_xCe_{1-x}O₂/H-ZSM5 (that for Mn_{0.8}Ce_{0.2}O₂ was 200 mg, which was mixed with trace amount of quartz sands to keep the mass of active phase consistency) was loaded into a glass wool packing. Reaction feed consisted of 1000 ppm CB, 142 mL/min N₂, 16 mL/min O₂ with a gas hourly space velocity (GHSV) at 10000 h⁻¹. Reaction temperature was monitored using a thermocouple loaded in the core of catalyst bed with the measuring range at 150–400 °C. All catalysts were sieved into 40–60 mesh. The concentration of CB and CO₂/CO production were analyzed on-line by using a chromatograph (GC, Agilent 6890, America) equipped with a flame ionization detector (FID), an electron capture detector (ECD) and a nickel converting equipment. Humid condition was achieved by bubbling the water using a N₂ flow to achieve the humidity at ca. 10 vol% (as measured by using the instrument of Hygrograph, Testo 480, Germany).

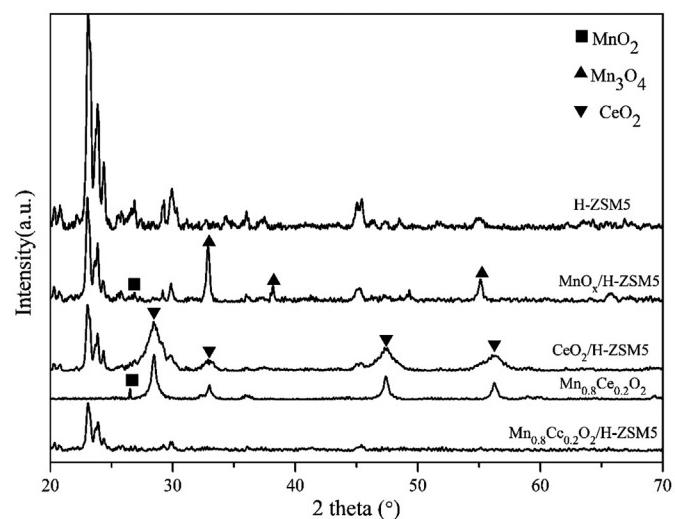


Fig. 1. X-ray powder diffraction patterns of Mn_xCe_{1-x}O₂/H-ZSM5 and Mn_{0.8}Ce_{0.2}O₂ catalysts.

2.4. By-products measurements

The off-gas (containing various gaseous products) was captured by using adsorption tube (Tenax TA/Tenax GR) at a set of temperatures for 30 min. The adsorbed compounds were then released in a thermal desorption instrument (TDI, PERSEE-TP7, PR China), which were injected into a GC/MS system (Agilent 7890A GC equipped with Agilent 5975C MS) equipped with a J&W113-4332GS-GasPro chromatographic column (America).

The concentration of Cl⁻ (as resulted from Cl₂) and ClO⁻ (as resulted from Cl₂ and HCl) was measured by using an ion chromatograph instrument (Shimadzu LC-20A, Japan), where 0.0125 M NaOH solution was used to absorb the off-gas for 30 min.

2.5. In situ DRIFT measurements

In situ DRIFT was conducted by using a Nicolet 6700 FTIR spectrometer equipped with a MCT detector. The DRIFT cell (Harrick) with CaF₂ windows was fitted into a heating cartridge that allowed the catalyst being heated up to 400 °C under atmospheric condition. In each measurement, the catalyst was first pretreated in a flow of He (99.99%, 100 mL/min) at the temperature of 400 °C for 1 h and then naturally cooled down to room temperature. Thereafter, 100 ppm CB together with a carrier gas of N₂ and O₂ of 10 vol% were introduced, followed by a series of heat-treatments to target temperature (heating rate at 10 °C/min). The spectra (average of 32 scans at 4 cm⁻¹ resolution) were simultaneously recorded.

3. Results and discussion

3.1. X-ray powder diffraction and BET surface area measurements

As reported by Wang et al. [1], the Mn_xCe_{1-x}O₂ catalyst with Mn/Mn + Ce molar ratio at ca. 0.78 had the highest activity in CB oxidation. Accordingly, a Mn_{0.8}Ce_{0.2}O₂ compound was selected herein as active phase to load onto H-ZSM5 carrier for subsequent study. Phase identities and purities of Mn_xCe_{1-x}O₂/H-ZSM5 and Mn_{0.8}Ce_{0.2}O₂ catalysts were analyzed by using X-ray powder diffraction (XRD), which were directly referenced with JCPDS patterns for peak assignments. As shown in Fig. 1, the H-ZSM5 revealed the characteristic peaks in the 2θ range of 20–30°. The loading of Mn or Ce oxide did not change the H-ZSM5 structure as these characteristic peaks were still retained in Mn_xCe_{1-x}O₂/H-ZSM5 cat-

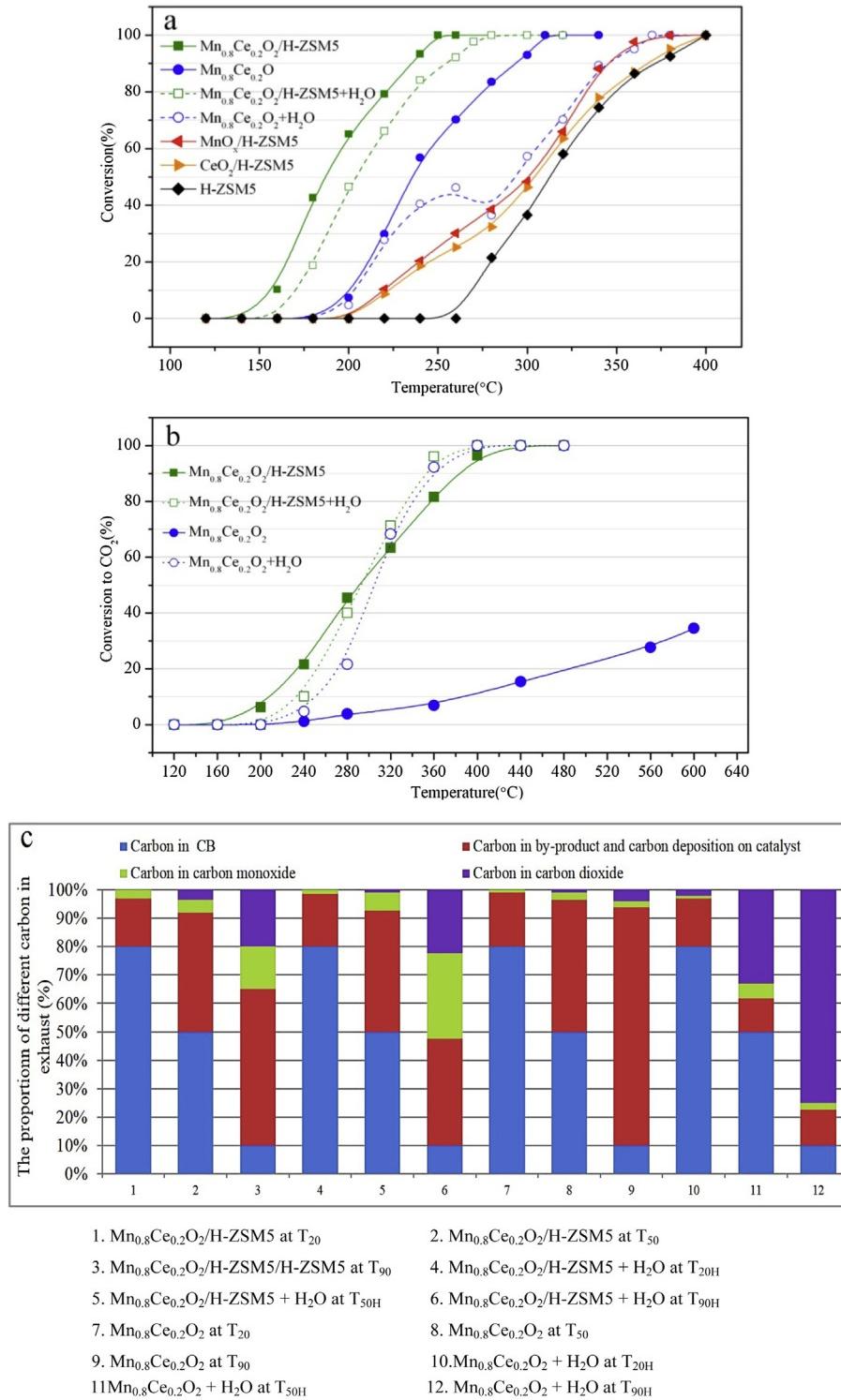


Fig. 2. (a) CB conversions over Mn_xCe_{1-x}O₂/H-ZSM5 and Mn_{0.8}Ce_{0.2}O₂ catalysts under dry condition; (b) mineralization rate analyses in CB oxidation over Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 and Mn_{0.8}Ce_{0.2}O₂ catalysts under dry and humid conditions; (c) carbon distributions in the out-let gaseous under different conditions. (reaction condition: gas hourly space velocity (GHSV) at 10,000 mL/(g h), CB at ca. 1000 ppm, N₂ flow rate at ca. 142 mL/min, O₂ flow rate at ca. 6 mL/min). Note: the T₉₀, T₅₀ and T₂₀ were the temperatures under dry condition and the T_{90H}, T_{50H} and T_{20H} were the temperatures under humid condition. The T₉₀, T₅₀, T₂₀ for Mn_{0.8}Ce_{0.2}O₂ were at ca. 300, 235 and 210 °C, respectively; the T_{90H}, T_{50H} and T_{20H} for Mn_{0.8}Ce_{0.2}O₂ were at ca. 340, 293 and 213 °C, respectively; the T₉₀, T₅₀ and T₂₀ for Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 were at ca. 230, 180 and 162 °C, respectively; the T_{90H}, T_{50H} and T_{20H} for Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 were at ca. 242, 200 and 180 °C, respectively.

alysts. The Mn oxide involved a Mn₃O₄ phase (JCPDS 18-0803 with the characteristic peaks at 2θ = 32.9°, 37.2° and 55.0°) and a MnO₂ phase (JCPDS 42-1169 with the characteristic peaks at 23.5°). The CeO₂ was with a cubic fluorite structure (JCPDS 34-0394), showing the characteristic peaks at 28.6°, 33.3°, 47.5° and 56.5°. The

Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 catalyst did not yield distinct characteristic peaks for either MnO_x or CeO₂, implying that these oxides might be highly dispersed over the H-ZSM5 support [30]. BET surface area measurements indicated that the Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 catalyst was with the surface area at ca. 250.0 m²g⁻¹ whilst that

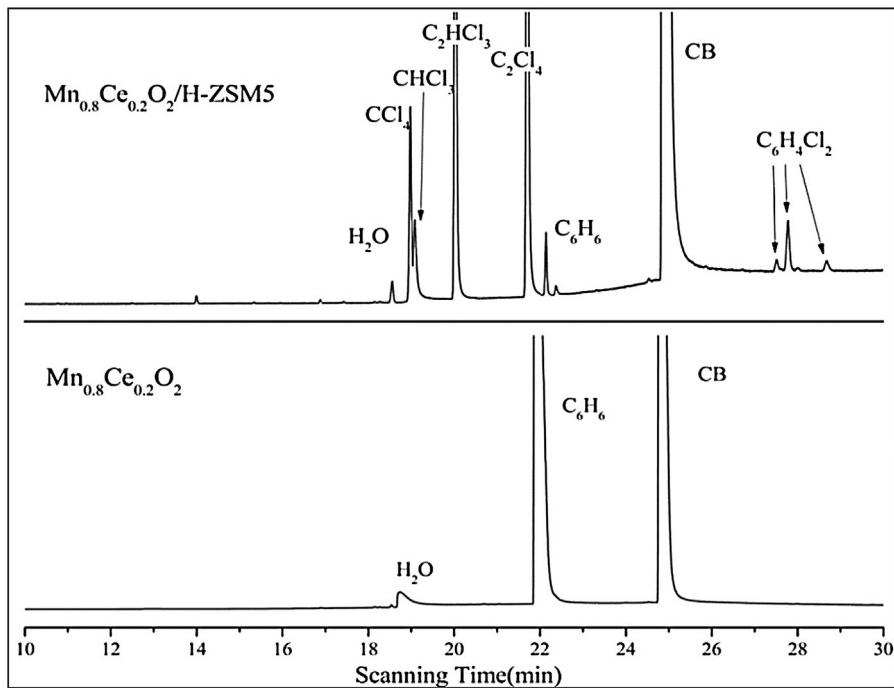


Fig. 3. GC/MS measurements on the off-gases from CB oxidation over $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2/\text{H-ZSM5}$ and $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2$ catalysts at their T_{90} under dry condition.

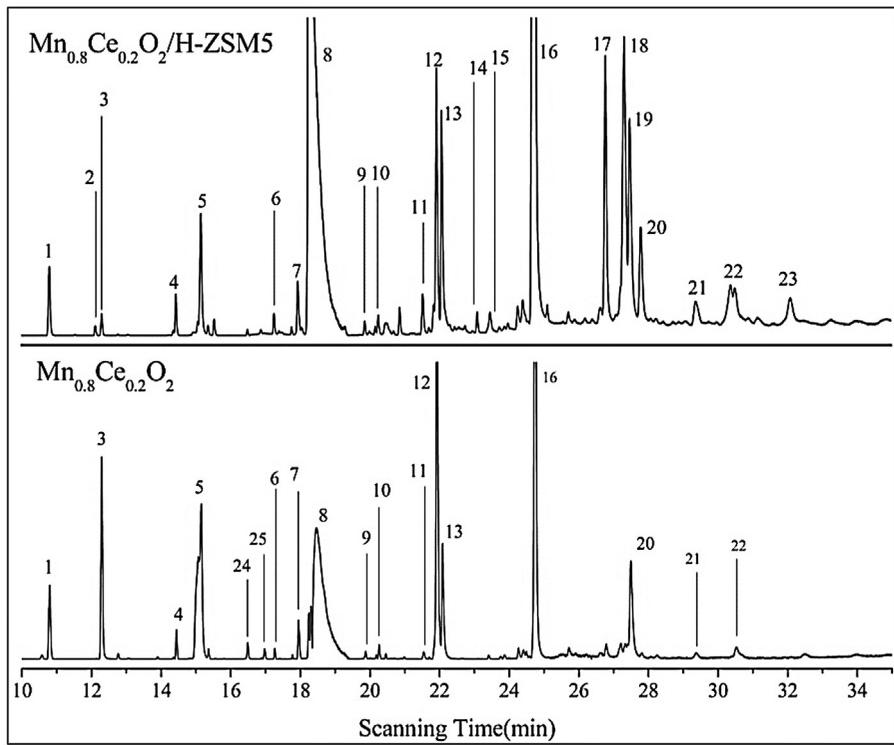


Fig. 4. GC/MS measurements on the off-gases from CB oxidation over $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2/\text{H-ZSM5}$ and $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2$ catalysts at their T_{90H} under humid condition.

for $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2$ was at ca. $247.0 \text{ m}^2\text{g}^{-1}$; for $\text{CeO}_2/\text{H-ZSM5}$ at ca. $270.0 \text{ m}^2\text{g}^{-1}$; for $\text{MnO}_x/\text{H-ZSM5}$ at ca. $243.4 \text{ m}^2\text{g}^{-1}$ and for H-ZSM5 alone at ca. $226.5 \text{ m}^2\text{g}^{-1}$.

3.2. CB conversion and CO_2 production analyses

In activity measurement, catalysts were all subjected to a feed stream containing 1000 ppm CB, 10 vol% O_2 and balanced

N_2 at the $\text{GHSV} = 10000 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$. As shown in Fig. 2a, the $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2/\text{H-ZSM5}$ catalyst revealed the highest activity in CB conversion. The light-off temperature, T_{50} (i.e. 50% CB conversion), measured for this catalyst was at ca. 180°C , which was much lower than those of $\text{MnO}_x/\text{H-ZSM5}$ and $\text{CeO}_2/\text{H-ZSM5}$ catalysts (their T_{50} were both at ca. 300°C). The result indicating that the co-existence of MnO_x and CeO_2 had induced a synergistic promotion in CB conversion, which was consistent with previous report [1]. For

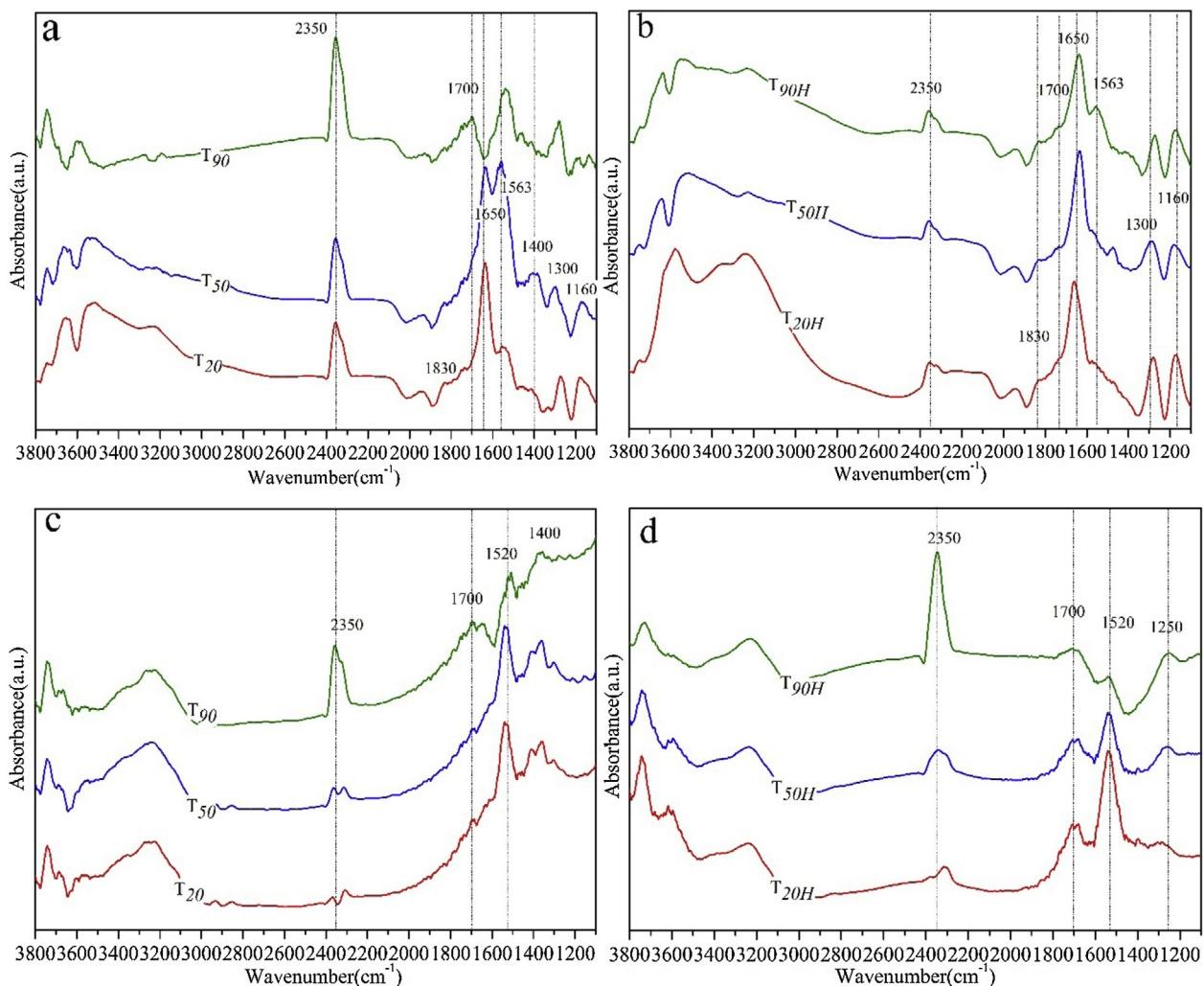


Fig. 5. In situ DRIFT spectra of CB oxidation over (a) Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 catalyst at T₂₀, T₅₀, T₉₀ under dry condition; (b) Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 catalyst at T_{20H}, T_{50H}, T_{90H} under humid condition; (c) Mn_{0.8}Ce_{0.2}O₂ catalyst at T₂₀, T₅₀, T₉₀ under dry condition and (d) Mn_{0.8}Ce_{0.2}O₂ catalyst at T_{20H}, T_{50H}, T_{90H} under humid condition.

Mn_{0.8}Ce_{0.2}O₂ catalyst, the T₅₀ was measured at ca. 235 °C, which was also higher than that of Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 catalyst, implying that the presence of H-ZSM5 had promoted the CB conversion over the supported catalyst [31].

Under humid condition (with ca. 10 vol% H₂O), the Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 catalyst yielded a slight deactivation in CB conversion, which was proposed due to the competitive absorption between H₂O and CB [32,33]. The Mn_{0.8}Ce_{0.2}O₂ catalyst however showed a severe deactivation when the measuring temperature was higher than 250 °C. As reported by Bertinchamps et al. [34], the H₂O steam could remove the Brønsted acid sites from catalyst surface. Since the oxidation of chlorinated hydrocarbons oxidation was generally initiated from their absorptions onto the Brønsted acid sites [35,36], the reduction in Brønsted acid sites would profoundly inhibit the CB oxidation over the Mn_{0.8}Ce_{0.2}O₂ catalyst. This also explained why the Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 catalyst possessed a much higher H₂O poisoning resistance than the Mn_{0.8}Ce_{0.2}O₂ catalyst as the H-ZSM5 would provide sufficient Brønsted acid sites for CB adsorption.

After measuring the CO₂ production in CB oxidation (see Fig. 2b), the Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 and Mn_{0.8}Ce_{0.2}O₂ catalysts both showed rather low CO₂ production rate at their T₂₀, T₅₀ and T₉₀. At ca. 230 °C (i.e. the T₉₀ for Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 catalyst), only ca. 20% CB was converted into CO₂ (see Fig. 2c). This was even worse for Mn_{0.8}Ce_{0.2}O₂ catalyst where the 20% CO₂ production was achieved

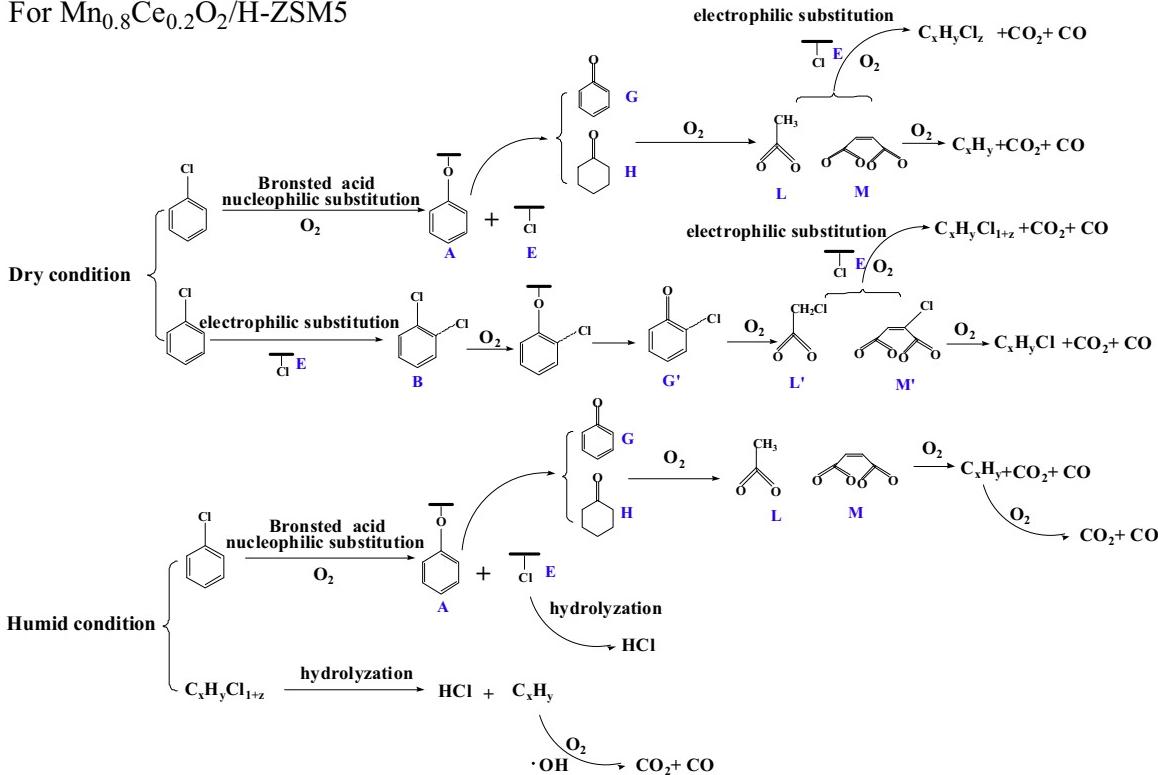
at the temperature as high as ca. 500 °C. There is no doubt that abundant by-products have been generated during CB oxidation. The CO₂ production result also indicated that the presence of H-ZSM5 could profoundly promote the CB mineralization over the Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 catalyst, which yielded ca. 90% CO₂ production at ca. 340 °C whilst that for Mn_{0.8}Ce_{0.2}O₂ catalyst was out of our measuring range (see Fig. 2b). Under humid condition, it was noted that the H₂O did not affect the CO₂ production over the Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 catalyst whilst for Mn_{0.8}Ce_{0.2}O₂ catalyst, a significant improvement in CB mineralization was observed, the reason of which will be interpreted in later section.

From the CO₂ production measurements, it was deduced that measurements solely on CB conversion was not appropriate as it did not reveal the actual performances for investigated catalysts. Studies onto CO₂ and HCl production, as well as intermediate by-products production were hence very necessary.

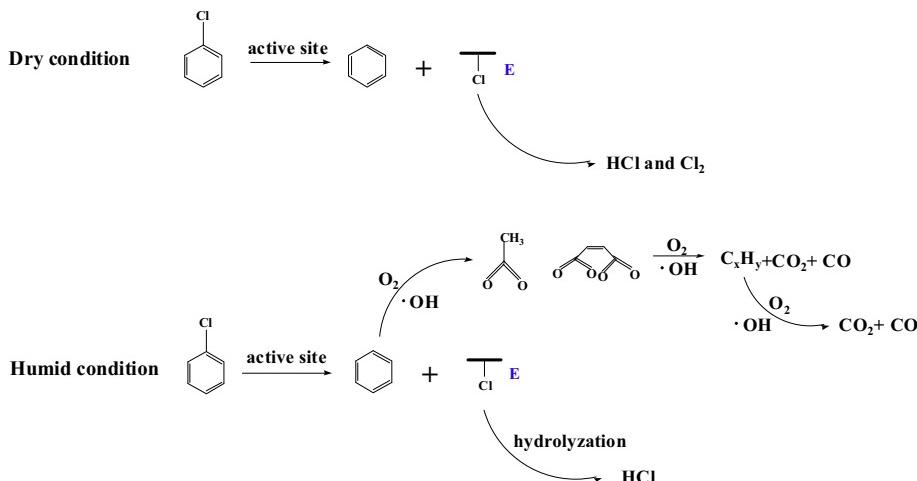
3.3. HCl and Cl₂ production

HCl and Cl₂ production were measured through bubbling the out-let gas stream into a 0.0125 M NaOH solution for 30 min at T₂₀, T₅₀ and T₉₀ for Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 and Mn_{0.8}Ce_{0.2}O₂ catalysts, respectively. An ion chromatography (IC) was employed to measure the amounts of ClO⁻ (as resulted from Cl₂) and Cl⁻ (as resulted from HCl) in solution. As shown in Table 1, the

For $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2/\text{H-ZSM}5$



For $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2$



Scheme 1. Proposed CB oxidation routes over $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2/\text{H-ZSM}5$ and $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2$ catalysts under dry and humid conditions. Note: this proposed mechanism was lack of the consideration on Cl_2 and H_2O production.

$\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2$ catalyst revealed a higher HCl production rate than the $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2/\text{H-ZSM}5$ catalyst under dry condition. This was unusual as the H-ZSM5 was expected to provide sufficient H^+ to induce more HCl production. One reason could be that the vast majority of dissociated chlorine had been converted into chlorinated by-products over the $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2/\text{H-ZSM}5$ catalyst (this had been confirmed in following GC/MS measurements). The Cl_2 production over $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2/\text{H-ZSM}5$ and $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2$ catalysts were both rare, which was only detected at the T_{50} and T_{90} for $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2$ and T_{90} for $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2/\text{H-ZSM}5$. As reported [37], in chlorinated hydrocarbons oxidation, the Cl_2 was generally produced at the temperature higher than 250°C due to the occurrence of Deacon reaction. In this study, the T_{20} , T_{50} and T_{90} (at ca. 230°C)

for $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2/\text{H-ZSM}$ catalyst were all lower than 250°C (see Fig. 2a), which was unsurprisingly given the lack of Cl_2 in CB oxidation.

Under humid condition, both $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2/\text{H-ZSM}5$ and $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2$ catalysts revealed profoundly enhanced HCl production where the Cl_2 production were effectively inhibited. The reason was due to the addition of H_2O could induce hydrolysis reaction that would enforce the dissociated Cl^\bullet to form HCl [32,38–40].

3.4. By-products generation in off-gases

To evaluate the by-products generation, GC/MS measurements were employed. The measurements were conducted under both

Table 1

HCl and Cl₂ productions in CB oxidation over Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 and Mn_{0.8}Ce_{0.2}O₂ catalysts under humid and dry conditions. Note: the T₉₀, T₅₀ and T₂₀ were the temperatures under dry condition and the T_{90H}, T_{50H} and T_{20H} were the temperatures under humid condition.

		Dry condition			Humid condition		
		T ₂₀	T ₅₀	T ₉₀	T _{20H}	T _{50H}	T _{90H}
Mn _{0.8} Ce _{0.2} O ₂ /H-ZSM5	HCl(ppm)	10.7	26.4	187.2	60.4	165.8	418.2
	Cl ₂ (ppm)	–	–	2.8	–	–	–
Mn _{0.8} Ce _{0.2} O ₂	HCl(ppm)	18.9	39.5	272.9	26.7	60.3	298.8
	Cl ₂ (ppm)	–	8.3	28.7	–	–	11.01

dry and humid conditions. The reaction temperature of T₉₀ for dry condition and T_{90H} for humid condition were selected to ensure the most conversion of CB that would produce sufficient by-products for measurements. In each measurement, the out-let gas was collected by using an adsorption column for 30 min. The column was then degassed in a thermal analyzer equipped with a GC/MS for analyses. As shown in Fig. 3, the Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 catalyst revealed the main products including CB, tetrachloromethane (CCl₄), trichloromethane (CHCl₃), dichloromethane (CH₂Cl₂), trichloroethylene (C₂HCl₃), tetrachloroethylene (C₂HCl₄), dichlorobenzene (C₆H₄Cl₂) and benzene (C₆H₆). The presence of chlorinated by-products explained why the Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 catalyst was with low HCl production than the Mn_{0.8}Ce_{0.2}O₂ catalyst (see Table 1) under dry condition as the vast majority of Cl[•] had been transferred into chlorinated by-products (e.g. CCl₄, CHCl₃, C₂HCl₄, etc.) during CB oxidation. The primary chain by-products also indicated that the aromatic ring of CB was effectively cracked over the Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 catalyst as the Mn_{0.8}Ce_{0.2}O₂ alone was lack of these chain by-products with only benzene being detected (see Fig. 3).

The presence of polychlorinated by-products, e.g. CCl₄, CHCl₃, C₂HCl₄, etc. further revealed that there was a chlorination reaction being occurred over the catalyst. Such reaction was proposed to be originated from an electrophilic substitution of dissociated Cl[•] over the Lewis acid sites of MnCl_x and CeCl₄ (as resulted from the reaction between Mn_{0.8}Ce_{0.2}O₂ and accumulated dissociated Cl[•] over H-ZSM5). Similar phenomena had been observed in FeCl₃, AlCl₃, SbCl₃, MnCl₂, MoCl₃, SnCl₄ and TiCl₄ catalysts, which also yielded significant polychlorinated by-products in catalytic oxidation of chlorinated hydrocarbons [18,41]. For Mn_{0.8}Ce_{0.2}O₂ catalyst, only benzene was detected, implying that the CB oxidation over this catalyst was initiated from the dechlorination of aromatic ring into benzene [38].

Under humid condition, a total of 25 by-products were detected for both Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 and Mn_{0.8}Ce_{0.2}O₂ catalysts (see Fig. 4 and Table 2). These by-products involved the vast majority of non-chlorinated chain by-products (e.g. C₄H₈, C₅H₁₀, C₆H₁₂, C₂H₄O, C₃H₆O, etc.). Only trace amounts of C₂HCl₃ and CH₃Cl were detected, implying that the dissociated Cl[•] had been transferred into HCl in the presence of H₂O, which was consistent with HCl production measurements (see Table 1).

From Fig. 4, it was also noted that unlike dry condition, the Mn_{0.8}Ce_{0.2}O₂ catalyst yielded primary chain by-products under humid condition. This indicated that the aromatic ring of CB was effectively cracked in the presence of H₂O. Aranzabal et al. had reported that the addition of H₂O could wash out the accumulated chlorine from the active sites of metal oxides, which effectively retain their oxidizing capacities and hence enhance the ring-opening of CB [42]. This might explain why the Mn_{0.8}Ce_{0.2}O₂ catalyst was with enhanced ring-opening ability under humid condition. The H-ZSM5 might also possess such prection function as H₂O did. Its abundant Brønsted acid sites could effectively absorb

Table 2

The products in the off-gases from CB oxidation over Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 and Mn_{0.8}Ce_{0.2}O₂ catalysts under humid condition.

Label	Molecular formula	Molecular structure	Name of Compound
1	C ₃ H ₆		Propylene
2	C ₄ H ₁₀		Butane
3	CH ₃ Cl		Methyl chloride
4	C ₄ H ₈		1,Butene
5	C ₄ H ₈		2,Butene
6	C ₅ H ₁₀		2,Pentene
7	C ₅ H ₁₀		1,Pentene
8	H ₂ O		Water
9	C ₆ H ₁₂		2,Hexene
10	C ₆ H ₁₂		1,Hexene
11	C ₂ HCl ₃		Trichloroethylene
12	C ₆ H ₆		Benzene
13	C ₂ H ₄ O		Acetaldehyde
14	C ₃ H ₄ O		Acrylic aldehyde
15	C ₃ H ₆ O		Propionaldehyde
16	C ₆ H ₅ Cl		Chlorobenzene
17	C ₈ H ₁₀		m-Xylene
18	C ₈ H ₁₀		o-Xylene
19	C ₈ H ₁₀		p-Xylene
20	C ₃ H ₆ O		Acetone
21	C ₅ H ₈ O		Pentene aldehyde
22	C ₄ H ₈ O		Butanone
23	C ₇ H ₈		Methylbenzene
24	C ₂ H ₃ Cl		Monochloroethane
25	C ₂ H ₂ Cl ₂		Dichloroethane

the dissociated chlorine to protect the Mn_{0.8}Ce_{0.2}O₂ from chlorine poisoning, which led to remarkable ring-opening ability for Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 catalyst (even under dry condition). The intrinsic physical and chemical properties of H-ZSM5 were also able to hinder the carbonaceous deposition on catalyst surface [43], which further enhanced the CO₂ production over the catalyst (see Fig. 2b).

In addition, the hydrolysis reaction as resulted from H₂O could provide sufficient H[•] to induce C_xH_yCl dechlorination into C_xH_{y+1} [6,18,38,43], which led to the formation of primary non-chlorinated by-products (e.g. C₄H₈, C₅H₁₀, C₂H₄O, C₃H₆O etc.) over both Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 and Mn_{0.8}Ce_{0.2}O₂ catalysts (see Fig. 4 and Table 2). At elevated temperatures, the H₂O might also generate hydroxyl free radicals (OH[•]) [44,45], which might induce a deep oxidation of CB into CO₂ due to the persisted high oxidizing capacity (see Fig. 2b for CO₂ production measurement for Mn_{0.8}Ce_{0.2}O₂ catalyst)[46,47].

3.5. In situ DRIFT measurements

To probe into CB oxidation routes, in situ DRIFT measurements were then employed. As shown in Fig. 5a, at T₂₀, the Mn_{0.8}Ce_{0.2}O₂/H-ZSM5 catalyst revealed a series of bands at ca. 2350, 1830, 1700, 1650, 1563, 1400, 1300 and 1160 cm⁻¹. The

band at 2350 cm^{-1} was assigned to the vibration of CO_2 [48]. Bands at 1830 and 1700 cm^{-1} were originated from the vibration of aldehyde-type species [49,50]. Bands at 1300 and 1160 cm^{-1} were corresponded to maleate related species (that might involve chlorine) [49,51,52] and bands at 1400 and 1563 cm^{-1} were originated from the asymmetric stretching of chlorinated acetate/acetyl halides. These chlorinated acetate/acetyl halides were not detected in GC/MS measurements (see Fig. 3), which were produced from CB ring-opening and would be quickly transferred into chlorinated chain hydrocarbons at elevated temperatures [50,53,54]. The band at 1650 cm^{-1} was assigned to C=O vibration of cyclohexanone or benzoquinone species [55–57], which were originated from the absorption of chlorinated benzene onto the Brønsted acid sites of H-ZSM5 via a nucleophilic substitution [51,58,59]. Since the aromatic ring in cyclohexanone or benzoquinone was much easier to be cracked than that in CB [51,58,59], the formation of which would effectively enhance the CB ring-opening over the $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2/\text{H-ZSM5}$ catalyst, leading to the production of primary-chain by-products over the catalyst (see Fig. 3). With increasing the measuring temperature, a decrease in the band at 1650 cm^{-1} and an increase in the band at 1563 cm^{-1} were observed. This indicated that the cyclohexanone or benzoquinone species had been oxidized into chlorinated acetate/acetyl halide at elevated temperatures. Under humid condition, the bands corresponding to chlorinated acetate/acetyl halide (at ca. 1563 cm^{-1}) were very weak (see Fig. 5b), implying that there were little chlorinated species being produced in the presence of H_2O , which was consistent with the GC/MS measurements (see Fig. 4 and Table 2).

For $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2$ catalyst, the DRIFT spectrum revealed the bands at ca. 2350 , 1700 , 1520 and 1400 cm^{-1} at the temperature of T_{20} . The band at 1700 cm^{-1} was corresponded to the vibration of aldehyde-type species and bands at 1400 and 1520 cm^{-1} were originated from the ring stretching of benzene [60,61], which was consistent with the GC/MS measurements (revealing that only benzene was detected in the off-gas, see Fig. 3). With increasing the measuring temperature, a decrease in the band at ca. 1520 cm^{-1} (corresponding to benzene) and an increase in the band at ca. 1700 cm^{-1} (corresponding to aldehyde-type species) were observed, which indicated that the benzene were oxidized into chain hydrocarbons at elevated temperatures. Under humid condition, the band at 1250 cm^{-1} (corresponding to CH_2 twists [50,53,62]) and at 1700 cm^{-1} (corresponding to aldehyde-type species) were appeared (see Fig. 5d), both of which were produced from CB ring-opening, revealing that the presence of H_2O had effectively promoted the CB ring-opening over the $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2$ catalyst, consistent with the GC/MS measurements (see Fig. 4 and Table 2).

3.6. Proposed oxidation mechanism

Based on the aforementioned analyses, the CB oxidation routes over $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2/\text{H-ZSM5}$ and $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2$ catalysts under dry and humid conditions were proposed in Scheme 1.

Under dry condition, for $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2/\text{H-ZSM5}$ catalyst, the CB was initially absorbed onto the Brønsted acidic sites of H-ZSM5 via a nucleophilic substitution. At this stage, the weaker C–Cl band (than the C–H band [51,63]) in aryl halides was first transferred into phenolates (A) [51,58,59] and then into benzoquinone (G) or cyclohexanone (H) species (as evidenced by DRIFT analyses in Fig. 5a). The (G) or (H) were oxidized into acetates species (L) and maleates (M) and eventually CO_2 and H_2O at elevated temperatures [51,58,59]. During CB oxidation, some CB were also transferred into dichlorobenzene (B) at the initial stage (as evidenced by GC/MS analyses in Fig. 3), which was achieved via a Lewis acid electrophilic substitution by dissociated Cl^\bullet (E). The (B) was then transferred

into (G'), which would crack the ring to form intermediate quinone species [5,6,25] at elevated temperatures. The quinone species were then oxidized into chlorinated acetates (L') and chloro-maleates (M') (see Fig. 5a,b) [7,51,58,59], that were further transferred into polychlorinated chain hydrocarbons. These chain hydrocarbons were then attacked by dissociated Cl^\bullet over the active sites of MnCl_x (or CeCl_x) via Lewis acid electrophilic substitution [18,41], resulting in the formation of polychlorinated by-products (e.g. C_2HCl_3 , CHCl_3 , etc., see Fig. 3) over the $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2/\text{H-ZSM5}$ catalyst.

Under humid condition, the CB ring-opening was still the initial stage for $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2/\text{H-ZSM5}$ catalyst as DRIFT analyses (see Fig. 5b) also showed the characteristic vibration bands of ring-opening products over the catalyst, e.g. chlorinated acetate/acetyl halide (at 1563 cm^{-1}) and maleate related species (at 1160 and 1300 cm^{-1}). However, the presence of H_2O had hindered the generation of chlorinated by-products due to the resulting hydrolysis reaction that would provide sufficient H to induce $\text{C}_x\text{H}_y\text{Cl}$ dechlorination into C_xH_{y+1} (see Fig. 4 and Table 2).

For $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2$ catalyst, since benzene was the main by-product, the CB oxidation route was initiated from the dechlorination of CB into benzene, which was then oxidized by active chemisorbed oxygen species into CO_2 and H_2O .

Under humid condition, the presence of H_2O had effectively enhanced the CB ring-opening over the $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2$ catalyst (see Fig. 4 and Table 2). This was proposed due to the removal of accumulated Cl^\bullet from the active sites of MnO_x or CeO_2 by H_2O washing. Furthermore, since the OH^\bullet radical was favorable to the formation of aldehyde species and the corresponding characteristic band (at 1700 cm^{-1}) were clearly observed in the $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2$ catalyst even at the temperature of $T_{20\text{H}}$ (see Fig. 5d), it was reasonable to propose that the active OH^\bullet radical (that was generated from the H_2O at elevated temperatures) had involved into the CB oxidation over the $\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_2$ catalyst, leading to a profoundly enhanced CO_2 production for the catalyst (see Fig. 2b).

4. Conclusion

In this paper, the role of H-ZSM5 in CB oxidation under both dry and humid conditions was explored. The CO_2 and HCl production and CB oxidation routes variation were evaluated. It was noted that the CB oxidation route was varied in the presence of H-ZSM5 and H_2O , which was deviated from the original Cl^\bullet dissociation into benzene to direct CB ring-opening, hence greatly promoting the CB oxidation performance over the catalysts. The work conducted herein evidenced that measurements solely on chlorinated hydrocarbons conversion were inappropriate as they did not reveal the actual performances for investigated catalysts. Studies onto CO_2 and HCl production and intermediate by-products production were hence very necessary. It is expected that this work could provide sufficient guideline for rational syntheses and design of reliable catalysts towards practical applications for catalytic oxidation of chlorinated hydrocarbons.

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